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(54) PRIMARY CELL AND POSITIVE ACTIVE MATERIAL MIX THEREFOR

(71) We, RHEINISCH-WESTFALISCHES ELEKTRIZITÄTWERK AG., a Company organised under the laws of the Federal Republic of Germany, of 43 Essen, Kruppstrasse 5, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention concerns a primary cell and a positive active material mix therefor. Known primary cells comprise a current conducting arrangement, and a mix comprising a positive active substance and a conducting additive in the form of graphite, the positive active substance and the conducting additive being thoroughly mixed.

In known primary cells and positive active material mixes, the conducting additive consists of graphite powder, carbon powder, or soot. The advantages derived from these with regard to electro-chemical utilisation of the positive active substance, in other words the positive depolarisation substance, are very slight. If manganese dioxide is used as the positive active substance, graphite powder is usually well mixed with the manganese dioxide and pressed in cylindrical shape around a central conducting pin, usually of graphite, as a so-called dolly.

Primary cells of this kind in cylindrical shape usually contain about 20–30 g manganese dioxide, of which only 15–20% is utilised electro-chemically, despite the fact that up to 20% of graphite powder is mixed in. In theory, 1.5 g manganese dioxide provides a depolarisation capacity of 1 Ah with a change in valence from manganese-IV to manganese-II. Single cells as primary cells with 30 g manganese dioxide provide only a maximum of 4 Ah even with a greatly extended form of discharge.

Further, graphite has been known for some time in the form of expanded graphite (see O. Vohler et al., "New kinds of car-

bons". Zeitschrift Angewandte Chemie, 82, No. 11, 1970 401–412). This has so far not influenced the problems relating to the construction of primary cells.

According to the present invention a primary cell comprises a positive active substance mixed with up to 25% by weight of expanded graphite and is pressed on to a current conducting arrangement.

The pressing of the mix should be sufficient to leave room for the cell electrolyte. The positive active substance may consist of manganese dioxide, lead oxide, or a mixture or a compound of both of these. Within the terms of the invention the mixing of the positive active substance and expanded graphite may be secured by mechanical means. However, another possibility lies in depositing the positive substance on the expanded graphite by chemical or physical deposition. Physical deposition includes evaporation, among other methods.

According to another aspect of the present invention, a primary cell positive active mix comprises a positive active substance mixed with up to 25% by weight of expanded graphite. Again, the positive active substance may be manganese dioxide, lead oxide, or a mixture or a compound of both of these.

Expanded graphite which, in a process not requiring to be discussed here in detail, is already technically obtained on a large scale, has a geometry fundamentally different from the normal graphite in sphere, flake or grain form. Expanded graphite is somewhat coral-like in texture. Expanded graphite is very light and extremely susceptible to change in form. This form change capability is made use of within the terms of the invention, when a pressing process is used. When the positive active substance in the form of powder is mixed in, the individual expanded graphite particles are changed in such a way that the particles of the positive active substance are firmly

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enclosed and will remain anchored in them. This thorough combination is enhanced by pressing. Pressing should, however, not be so intensive as to obliterate any interstices for the electrolyte. This lesser degree of pressing is the kind referred to in the invention.

The mixing of the expanded graphite with powdered positive active substances can be undertaken in various ways. As well as by dry mechanical mixing of a powdered positive active substance with the expanded graphite, the positive depolarisation substance may also be produced by combining the expanded graphite with the positive active substance by chemical or electrochemical deposition methods. For example, the expanded graphite can, initially, be wetted with a concentrated aqueous solution of manganese (II) nitrate and subsequently be dried carefully. When sufficient manganese nitrate is found on the surface of the particles of expanded graphite, this preliminary preparation is subjected to thermal disintegration at about 300°C. This results in the formation of finely distributed and highly active manganese dioxide in excellent combination on the surface of the expanded graphite. This process may be repeated several times until a required amount of positive substance has been combined with the expanded graphite. Another method would be the chemical precipitation of manganese hydroxide and subsequent conversion on, the expanded graphite into positive substance.

The primary cell according to the invention can be of the usual classical type with central carbon pin and a pasty ammonium chloride electrolyte. The term primary cell within the terms of the invention also covers a zinc/manganese dioxide system with sulphuric or phosphoric liquid electrolyte. For the current conducting arrangement for the positive electrode, copper, nickel, lead, lead-covered refined steel or titanium can be used, instead of the usual graphite or other synthetic carbon products. Tinned sheet, foil, mesh or conducting fibre felt are possible forms of the conducting arrangement.

The advantages achieved with primary cells and positive active material mixes according to the invention manifest themselves in a considerable improvement of the electrochemical utilisation of the positive active substance. In the case of manganese dioxide, 70% and more has been achieved. It can be assumed that the reason for this is the rather greater number of contact points of the individual expanded graphite particles, due to their considerably more expanded geometry, with the neighbouring expanded graphite particles. This increases the internal electrical conductivity of the positive active substance or depolarisation

substance. The deformation capability of the expanded graphite when this is mixed with the positive active substance powder further guarantees a close combination which is maintained also during use (discharge). This last feature does not occur at all with normal graphite, with soot or with other powdered carbon products as conducting additive. It is now possible with the use of expanded graphite to extract strong discharge currents also from a zinc/manganese dioxide cell without any marked polarisation. This means that with the appropriate construction a primary cell can be developed also for traction purposes.

Example of an embodiment

A weighed amount of 1.0 g expanded graphite is added to a roughly 30% solution of manganese nitrate. For wetting purposes it is advisable to add to the manganese solution approximately 5% alcohol (methanol, ethanol, butanol, isopropanol). The mixture is lightly stirred and then filtered. It is left to dry and then the crystals formed by the manganese nitrate on the surface of the expanded graphite material are disintegrated by heating at about 300°C. After cooling, the preparation weighs a total of 9 g. This indicates that an amount of 8 g MnO₂ has been added. The positive active material mix thus prepared is subsequently pressed around a graphite conducting pin to form an electrolyte-permeable tube (membrane) around the pin. The pressing should only be sufficient to allow sufficient porosity for the introduction of the electrolyte. The electrode thus prepared is connected in sulphuric acid of 1.2 specific gravity to a previously amalgamated zinc electrode. With a discharge of about 10 Ah this results in an average discharge terminal voltage of 2 Volts. The no-load voltage of the zinc/manganese dioxide combination in s.g. 1.2 sulphuric acid is above 2.2 V. From the amount of MnO₂ used and the capacity obtained it can be calculated that 70% of the depolarisation capacity of the manganese dioxide is utilised. The calculation is based on a theoretical value of 1.64 g MnO₂/Ah.

WHAT WE CLAIM IS:—

1. A primary cell comprising a positive active substance mixed with up to 25% by weight of expanded graphite, and is pressed on to a current conducting arrangement.
2. A primary cell as claimed in Claim 1 wherein the positive active substance is manganese dioxide.
3. A primary cell as claimed in Claim 1, wherein the positive active substance is lead oxide.
4. A primary cell as claimed in Claim 130

- 1, wherein the positive active substance is a mixture of manganese dioxide and lead oxide.
- 5 5. A primary cell as claimed in Claim 1, wherein the positive active substance is a compound of manganese dioxide and lead oxide.
- 10 6. A primary cell as claimed in any preceding Claim when the positive substance is deposited on the expanded graphite by chemical, electrochemical or physical deposition.
- 15 7. A primary cell as claimed in Claim 6, wherein deposition is effected by evaporation.
- 20 8. A primary cell, made according to the example.
9. A primary cell positive active material mix, comprising a positive active substance mixed with up to 25% by weight of expanded graphite.
10. A mix as claimed in Claim 9, wherein the positive active substance is manganese dioxide.
11. A mix as claimed in Claim 9, where- 25 in the positive active substance is lead oxide.
12. A mix as claimed in Claim 9, where- in the positive active substance is a mixture of manganese dioxide and lead oxide.
13. A mix as claimed in Claim 9, where- 30 in the positive active substance is a compound of manganese dioxide and lead oxide.
14. A mix as claimed in Claim 9, where- in the positive active substance is deposited on the expanded graphite by chemical, elec- 35 trochemical or physical deposition.
15. A mix as claimed in Claim 9, where- in deposition is effected by evaporation.
16. A positive active material mix made according to the example. 40
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